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Flammability, degradation and structural characterization of fibre-forming polypropylene containing nanoclay-flame retardant combinations

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Abstract

We have shown previously that the introduction of nanoclays can reduce the flammability of synthetic fibre-forming polymers like polyamides 6 and 6.6 only if used in conjunction with conventional flame retardants. In this work we report initial studies of the effects of dispersed nanoclays with low concentrations of selected flame retardants introduced into polypropylene on flammability, thermal degradation and X-ray diffraction behaviours. Flame retardants used include ammonium polyphosphate as a conventional char –former and a hindered amine stabiliser known to have flame retarding characteristics in polypropylene.

Key words: Flammability, polypropylene, nanoclays ammonium polyphosphate, hindered amine stabiliser

1. Introduction

Polypropylene was the first synthetic stereo-regular polymer to achieve industrial importance and it is presently one of the fastest growing fibres for technical end-uses where high tensile strength coupled with low-cost are essential features [1]. Polypropylene fibres have been widely used in many areas, such as apparel, upholstery, floor coverings, hygiene medical, geotextiles, car industry, automotive textiles, various home textiles and wall-coverings [2]. Because of its wholly aliphatic hydrocarbon structure, polypropylene by itself burns very rapidly with a relatively smoke-free flame and without leaving a char residue. It has a high self-ignition temperature (570°C) and a rapid decomposition rate compared with wood and other cellulosic materials and hence

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has a high flammability [3]. The heat of combustion for polypropylene was reported by Einsele et al. [3] to be 40 kJ/g and this is higher than many other simple fibre-forming polymers. In recent years, improvement in flame retardancy of the fibre-forming polymers including polypropylene has become increasingly important in order to comply with the safety requirements of textile products [4].

In parallel, nanocomposites have attracted considerable interest by the flame retardant polymer community since 1997 due to their improved fire properties [4-9]. It has been suggested that the presence of clay in a polymer can enhance the char formation providing a transient protective barrier and hence slowing down the degradation of the matrix [5, 6]. For instance, characterization of the flammability properties of a variety of polymer–clay nanocomposites including those containing polypropylene, under fire-like conditions, using the cone calorimeter [10] has revealed improved flammability properties in terms of reduced peak heat release rates. However, the presence of dispersed nanoclay often decreases times to ignite and so does not show a normal flame retardant behaviour. While the introduction of conventional flame retardants to polypropylene is possible, high concentrations are required even for quite modest levels of flame retardancy in comparison with other fibre-forming polymers. However, notwithstanding this problem, the challenge of flame retarding synthetic fibres in general is significantly higher than for bulk polymers because of their high surface area to volume ratio and the low tolerance to high filler loadings in the fibre production process. We have shown that use of nanoclays in polyamides 6 and 6.6 in conjunction with conventional flame retardants enables lower concentration of the latter to be used which still maintaining acceptable levels of flame retardancy [11, 12]. One major aspect from these earlier studies and those ongoing is that if maximum opportunity is to be gained from nanoclay inclusion, it is necessary to ensure a maximum dispersion of the nanoclays. Furthermore, it is essential to understand the effect that introduction of nanoclays has on polymer and hence fibre fine or nanophysical structure.

This work investigates the possibility of improving the flammability of isotactic polypropylene by using selected nanoclays in conjunction with both ammonium polyphosphate and a hindered amine stabiliser reported to have flame retarding properties in polypropylene [13]. Furthermore, the effect on both thermal degradation and polymer

physical structure are also reported. It has been expected that this study could improve the flammability of fibre-forming polypropylene yarn products from cooperation partners.

2. Materials and Experimental

2.1. Materials

The fibre-grade polypropylene suitable for technical yarns was provided by a UK fibre extruder. Three potentially flame retardant additive species were introduced to the polymer:

The functionalised nanoclay Cloisite® 30B was provided by Southern Clay Products, Inc. having the generic quaternary methyl, bis(dihydroxyethyl), hydrogenated tallow ammonium cation as functionalising species.

Ammonium polyphosphate (FR1) with commercial name of Antiblaze MCM was provided by Albemarle Corporation.

The hindered amine Flamestab® NOR116 (FR2) provided by Ciba Speciality Chemicals and reported to have flame retarding properties in polypropylene. NOR 116 is a hindered amine base on NOR functionalisation [13]. The mechanism by which it confers flame retardancy has not been reported but may be associated with its radical interacting, antioxidant character.

2.2. PP nanocomposite compounding

A Brabender W50E chamber fitted with cam blades was used to compound the polymer with nanoclay and other additives at a rotor speed of 60 rpm, set temperature of 190°C and a 6 min. mixing time. The polymer and all the additives were well mixed in a sample cup by shaking for 3 min. just before compounding. The optimised formulations designed by Maxsuite 99 software for compounded samples are shown in Table1, with the maximum concentration of clay and FR1 held constant at 5phr. This maximum value was deemed to be an upper limit concentration if any potential use in extruded fibres was to be considered. Addition of FR2 at 1phr was deemed to have negligible effect on fibre properties [14]

2.3. PP Film formation by compression moulding

Films (ca. 0.3mm thickness) were prepared from the blends by compression moulding with spacer plates, between aluminium foil-coated steel plates at a set plate temperature of 190°C. A pure PP control with equivalent thermal history to the filled samples was also produced.

2.4. Flammability testing:

Limiting oxygen index (LOI) values were determined on selected PP nanocomposite film samples with thickness of around 0.3mm by using a standard procedure [15].

2.5. Thermo gravimetric analysis

The TGA curves were obtained by using a Polymer Laboratories TG 1000 instrument under flowing air at a rate of 8cm^3/min with a heating rate of 20^{0}C/min. Approximately 6 mg samples were used in each case.

2.6. Gas analysis

The concentrations of carbon monoxide and carbon dioxide evolved from TG furnace were monitored by using a non-dispersive infrared gas analyser and the concentration of oxygen was monitored by using an electrochemical cell oxygen sensor. The TG furnace and the gas analyser cell was connected by an unheated line.

2.7. X-ray diffraction

X-ray diffraction analysis of compounded samples was carried out with a Siemens D500 X-ray Diffractometer with Cu-Kα radiation. The diffractometer was equipped with a diffracted beam graphite monochromator, tuned to Cu-Kα radiation, and a scintillation detector. Diffraction patterns were collected in reflection-mode geometry from 2° to 20° 2θ at a rate of 2° 2θ/min.

3. Results and Discussion

3.1. Flammability testing results

LOI values for PP control and compounded samples are shown in Table 1, and it is seen that there is no obvious change for sample PP2 where functionalised clay is the sole additive at 5 phr level. LOI is slightly increased in sample PP3 where the phosphorous-containing APP, FR1, is present along with the clay, each at 2.5 phr. This low concentration of APP would not be expected to produce significant increased flame retardancy to polypropylene since, normally, levels of 15 phr or higher are required [4]. However, on replacing FR1 by FR2, the LOI value (sample PP4) reduces to 18.7 below that from the control sample value of 19.2. While the error associated with the LOI technique is about ±0.5 LOI unit, this may suggest that the hindered amine itself has a negligible effect on the burning properties of polypropylene-clay compounded samples in terms of the LOI burning model offered by a vertically orientated sample ignited at the edge. The formulation with the highest LOI value of 22.1 in Table 1 is sample PP5, in which clay, FR1 and FR2 are all present in the composite. Comparing this result with those for samples 3 and 4, it is suggested FR2 may act as a synergist to FR1 in presence of the clay.

3.2. TG analysis

Figure 1 shows the TG curves in air for the PP control sample and two PP clay-containing samples. The starting degradation temperature for PP control sample is 259°C while for samples PP2, PP3, PP4 (see figure 4) and PP5, they are 266°C, 282°C,307°C and 297°C respectively. TG results show that the addition of FR1 or FR2 alone decreases the starting degradation temperature; hence the presence of nanoclay combined with FR1 and FR2 may be the main reason for the increased starting degradation temperature.

The char residues in air at 600°C are shown in Table 1. Values for samples PP2 and PP4 are 4.31 and 4.82% respectively are due to mainly the respective 5phr additions of nanoclay. For sample PP3, the char residue value of 3.21% is higher than the clay concentration of ca. 2.5%, which means the presence of FR1 can promote some char formation; this would be expected for ammonium polyphosphate and similar flame retardants [4]. For sample PP5, the char residue rises to 5.69%, and it is well above the

corresponding clay concentration of ca. 2.5%. Theoretically and experimentally, little or no char residue should exist for either FR1 or FR2 by themselves heated to 600^{o}C. It is suggested, therefore, P-N synergism between FR1 and FR2 could be the main contribution for the increase of the char residue of sample PP5, which has been further proved by the following gas analysis result.

3.3. Gas analysis

In attempts to determine the effects of clay and flame retardants on polypropylene degradation and oxidation, concentrations of oxygen, carbon monoxide and carbon dioxide in the atmosphere surrounding pyrolysing samples have been monitored during TG analysis. Because the gases were monitored outside the furnace of the TG instrument as described above, the gas concentration cannot give the instantaneous figure in the furnace due to the time required by the gases to travel from the furnace to the analyser. However, it can give us a delayed figure of gas concentration variation. The time delay has been measured by using a 1cm^3 syringe to inject standard CO_2 gas into the furnace evenly over a period of 1min and this has been observed to be 98 s (see Figure 2).

Figure 3 shows the percentage gas concentrations in volume as functions of temperature for the control PP1 sample. The ambient flowing oxygen concentration drops from 255^{o}C onwards and does not fully recover back to the original level until the sample temperature reaches 598^{o}C. Conversely the peak oxygen consumption occurs at 406^{o}C. It is observed also (see Figure 3) that most rapid volatilisation of polypropylene occurs over the range of 268^{o}C and 380^{o}C.

The monitored CO has a single peak at around 398^{o}C and the CO_2 response shows two peaks at 441^{o}C and 535^{o}C for the control sample. These observations suggest that volatiles formed up to 380^{o}C are oxidised or formed in parallel with CO; subsequent oxidation of the latter and other volatiles occurs at higher temperatures.

Figure 4 shows the percentage variation of gas concentrations with the temperature for the sample PP5 containing clay and both flame retardants. Here, the flowing air oxygen concentration drops from a higher temperature of 313^{o}C and does not fully recover to the original level until 613^{o}C with peak oxygen consumption occurring at 485^{o}C. Similarly, the single volatilisation stage is between 292^{o}C and 436^{o}C maximising at around 390 ^{o}C

which is higher than that of control sample. Furthermore, CO has a single peak at around 461^{o}C and the CO_2 response has one peak at around 494^{o}C suggesting shifts to higher temperatures for both gases in the presence of all three additives.

When the clay and hindered amine (FR2) are present together in sample PP4, Figure 5 shows the gas concentrations behaving in a manner similar to sample PP5 in that the ambient oxygen concentration drops from 314^{o}C onwards, recovering back to the original level at about 640^{o}C. The peak oxygen consumption occurs at a similarly higher value of 453^{o}C with the main volatilisation period between 307^{o}C and 427^{o}C, which is also higher than that of control sample. Again CO generation has a higher single peak temperature at around 439^{o}C with the CO_2 single peak around 464^{o}C. These results suggest that the hindered amine FR2 has some antioxidant character (compare samples PP4 and PP5) which is enhanced by accompanying char-formation of APP (FR1) in PP5, which is the further evidence for P-N synergism between FR1 and FR2 of sample PP5 .

In order to investigate the oxidation or degradation mechanism further, peak oxygen consumption values per mg and peak CO values released per mg sample have been calculated and are shown in Table 2. It is evident that although the clay-containing samples PP2 and PP4 have lower oxygen peak consumption values than that of the control sample, sample PP5 has a higher oxygen peak consumption value. However, the CO release peak values for clay-containing samples are not less than that of the control sample, both in the presence and absence of FR1 and FR2. Samples PP1 to PP4 are similar while sample PP5 has a CO release value almost twice these values. Furthermore, the released CO_2 peak values for clay-containing samples are all less than that of the control sample as are the respective CO_2 /CO values. This suggests that although the clay-containing samples have higher degradation temperatures, volatile oxidation is not as fully complete as in the control sample PP1, hence more CO and less CO_2 have been produced.

3.4. XRD characterization

The diffraction patterns for clay alone and selected PP compounded samples with the same thickness of 0.3mm are displayed in Figure 6. The clay (Cloisite 30B) itself has a

single peak at around 5.0° corresponding to a d-spacing of 1.7 nm. The clay-containing samples all have shifted clay peaks in addition to characteristic polypropylene crystallinity diffraction peaks (see Figure 6). The peaks around $2\theta = 6.0°$ with d-spacing of about 1.4 nm correspond to the clay characteristic peaks, and the shifts from 5.0° to 6.0° suggest the samples have lower d-spacings than that in the clay alone. This suggests that the clay-containing samples do not have expanded or intercalated lattices. In order to observe whether heat treatment experienced during compounding influences clay diffraction patterns the XRD patterns for clay itself before and after heating at 190°C for up to 10min were recorder (see Figure 7). It is seen that there is no clay peak position shift after heating which indicates that the functionalising groups have not been oxidised or destroyed after heating at 190°C for up to 10min. However, in the presence of polymer, it might be suggested that the attraction forces between the functionalising groups and clay are weakened by the extrusion process at 190 °C and the functionalising groups have partly or completely left the clay surfaces and diffused into the polymer phase, and hence the decreased d-spacing has been observed. Considering the natural montmorillonite clay typified by Cloisite Na+ with a d-spacing of 1.17nm [14], if all the functionalising groups have left clay surfaces and galleries and gone to the polymer phase, polypropylene intercalated structures with d-spaces of 1.4nm might have been achieved. However, if the functionalising groups have partly left clay galleries, it would be very difficult to determine whether the intercalated structure has achieved or not. It has been reported the addition of MAPP (maleic acid modified polypropylene) would be helpful to form a PP/clay nona-structure [16] and this will be discussed in our next publication involving PP grafted with different monomers. Comparing the clay XRD peaks of samples PP2, PP3 and PP5 which have the same amount of clay (2.5phr), the respective peak intensities are in the order PP3>PP2>PP5 and the peak from PP5 has the lowest 2θ value and hence largest d-spacing. This suggests that the clay in sample PP5 may have a relatively better dispersion with some exfoliation than in samples PP3 and PP2, and this may be the main reason why sample PP5 has the better fire performance and highest char residue, and this has been further confirmed by the optical transmission microscopy pictures shown in figure 8. Clay aggregates using optical microscopy have been observed in samples without FR2 (samples PP2 and PP3) indicating poor clay

dispersion while none have has been observed in the samples with FR2 (PP4 and PP5) indicating a much better clay dispersion.

While the XRD responses in Figure 6 were derived from samples of the same thickness, it is instructive to note whether or not slight changes in thickness influence XRD peak intensities and diffraction angles. Figure 9 shows the effect of sample thickness on the intensity of the XRD pattern (0.1 mm and 0.3 mm respectively). There are four peaks between 2θ values between 12° and 20° for each clay-containing sample, and these are related to the crystallinity of polypropylene present. The sample with the thickness of 0.3 mm has much higher intensity than the sample with the thickness of 0.1 mm as expected because x-rays are diffracted by more clay particles. The intensity of the clay peak with 6105 counts for the thicker sample is more than double the intensity of the clay peak with 2557 counts for the thinner sample. It is concluded, therefore, that if the sample thickness is within the penetration range of the x-rays used in the experiment, then samples having slight variations in thickness will yield similarly dependent diffraction intensities apart from other variables. However, the thickness of the sample will not affect the position of the peak, especially the correspondent clay peak. It is suggested that the thickness for series samples used in the XRD diffraction experiment should be kept as similar as possible as was the case for the sample patterns in Figure 6.

It should be noted that XRD patterns provide only indicative evidence that nanocomposite structures either as intercalated or exfoliated exist in a given polymer matrix. Transmission electron microscopy is usually required to substantiate; unfortunately, TEM was not available for this study and hence the above XRD result interpretations are indicative only.

4. Conclusions

The flammability of polypropylene can be reduced by the addition of small amounts of clay in conjunction with conventional phosphorus and a hindered amine flame retardants due to the possible P-N synergism. The LOI value for the improved formulation is 22.1 with only 6% loading, signifying a rise of 2.9 LOI units with respect of pure polymer. For polypropylene, this represents a significant increase in flame retardancy when more

conventional flame retardants at higher concentrations generate LOI values of 23 and slightly higher [4]. The compounded clay-containing PP samples may have intercalated structure and/or partly exfoliated structures and further investigation is required for a better understanding to the degradation mechanism of these as well as confirmation of the possible nanostructures present using TEM.

Acknowledgements

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Tables:

Table 1. Maximized formulations designed by Maxsuite 99 software with respective LOI values and char residues at 600 ^{o}C

No.	Clay (phr)	FR 1(phr)	FR2 (phr)	PP (phr)	LOI	Char residue at 600 ^{o}C
PP1	0	0	0	100	19.2	0.0
PP2	5	0	0	100	19.3	4.31
PP3	2.5	2.5	0	100	20.6	3.21
PP4	5	0	1	100	18.7	4.82
PP5	2.5	2.5	1	100	22.1	5.69

Table 2 Gas concentrations evolved per unit sample

No.	Clay (phr)	FR1 (phr)	FR2 (phr)	O_2 (%/mg)	CO (%/mg)	CO_2 (%/mg)	Ratio of CO_2 /CO
PP1	0	0	0	0.75	0.14	0.25	1.78
PP2	5	0	0	0.55	0.14	0.16	1.14
PP3	2.5	2.5	0	0.61	0.15	0.14	0.93
PP4	5	0	1	0.68	0.16	0.14	0.88
PP5	2.5	2.5	1	0.95	0.29	0.19	0.66

Figures

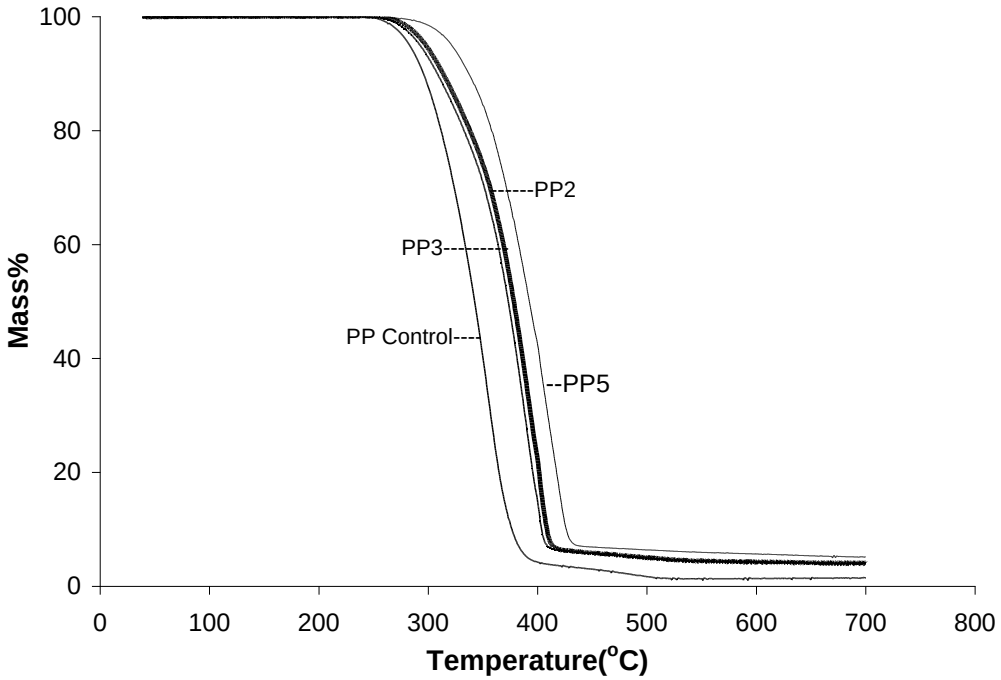

Figure 1 TG curves for PP control sample and PP compounded samples PP2, PP3 and PP5

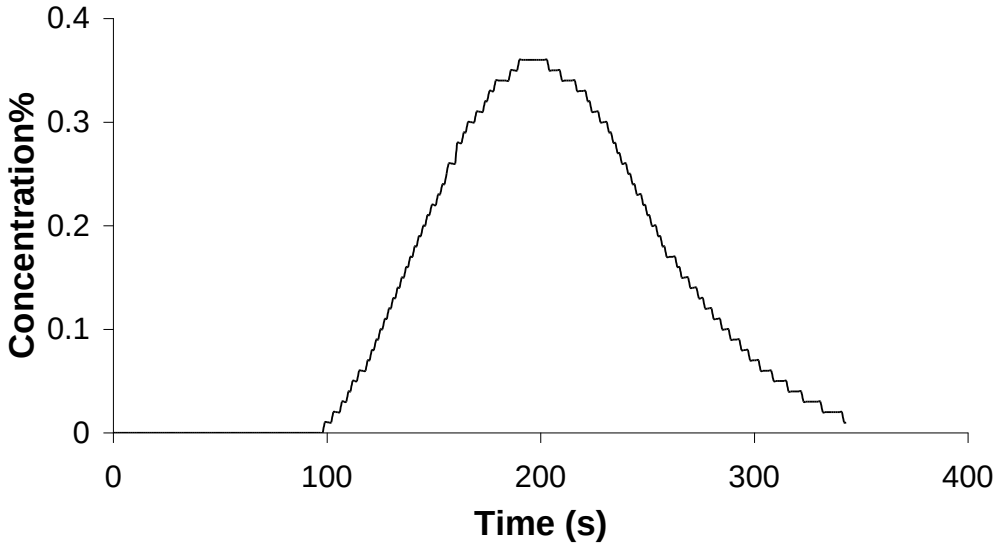

Figure 2 Time delay correction curves (CO_2 concentration monitored by the analyser); time = 0 s represents the point of gas sample injection into the TG furnace.

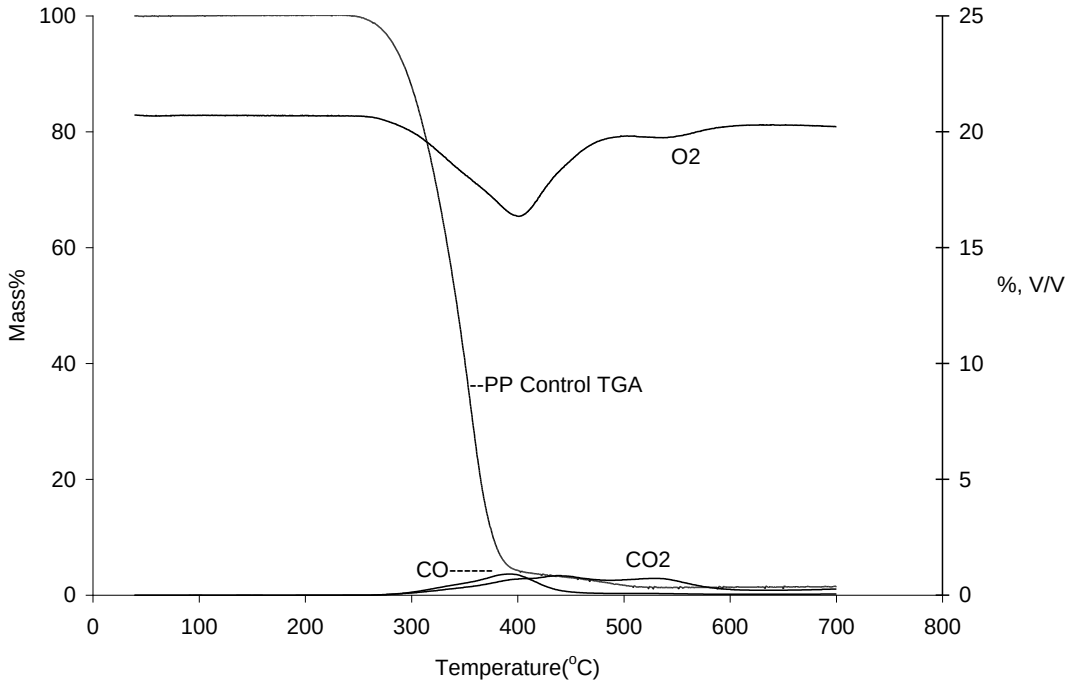

Figure 3 TGA response and gas concentration curves of control PP sample

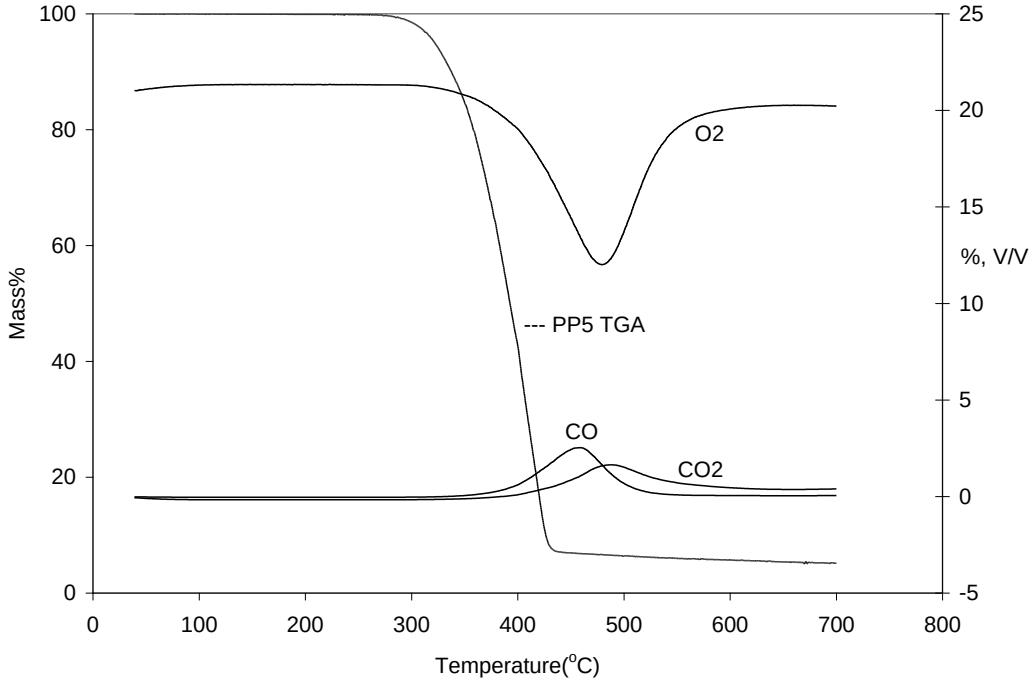

Figure 4 TGA response and gas concentration curves of sample PP5 containing clay, FR1 and FR2

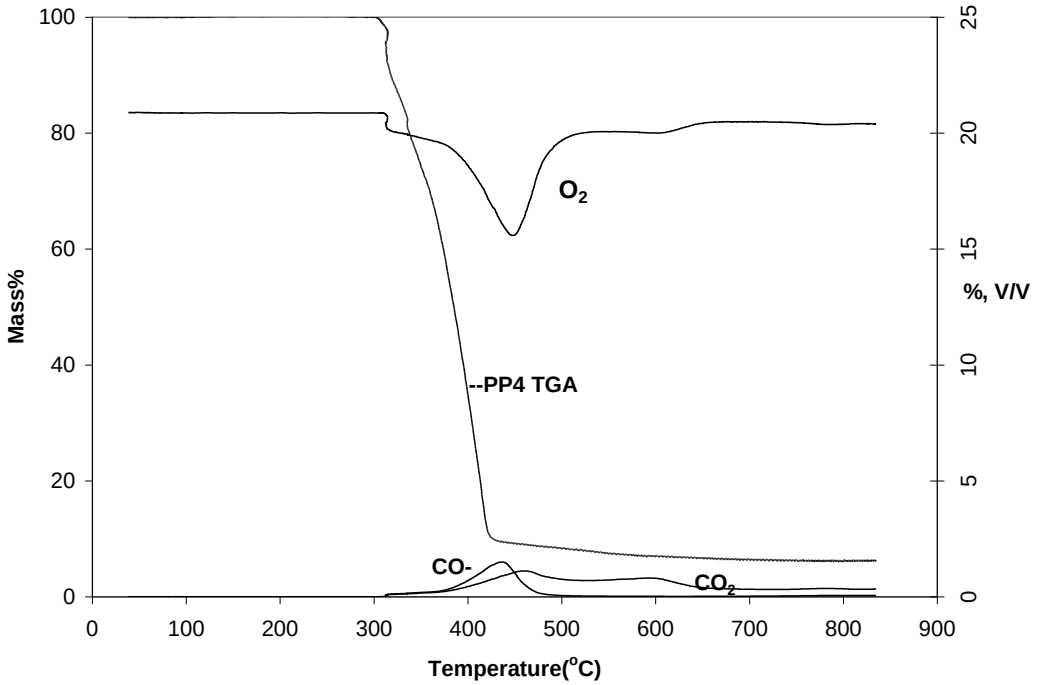

Figure 5 TGA response and gas concentration curves of sample PP4 containing clay and hindered amine (FR2) only

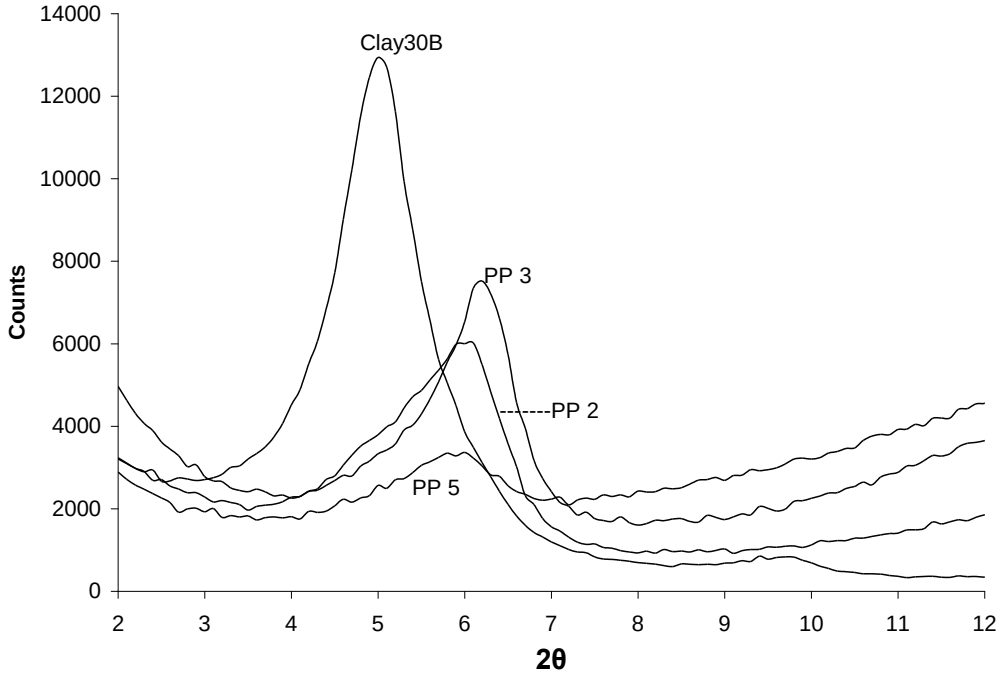

Figure 6 XRD patterns for clay and compounded samples PP2, PP3 and PP5

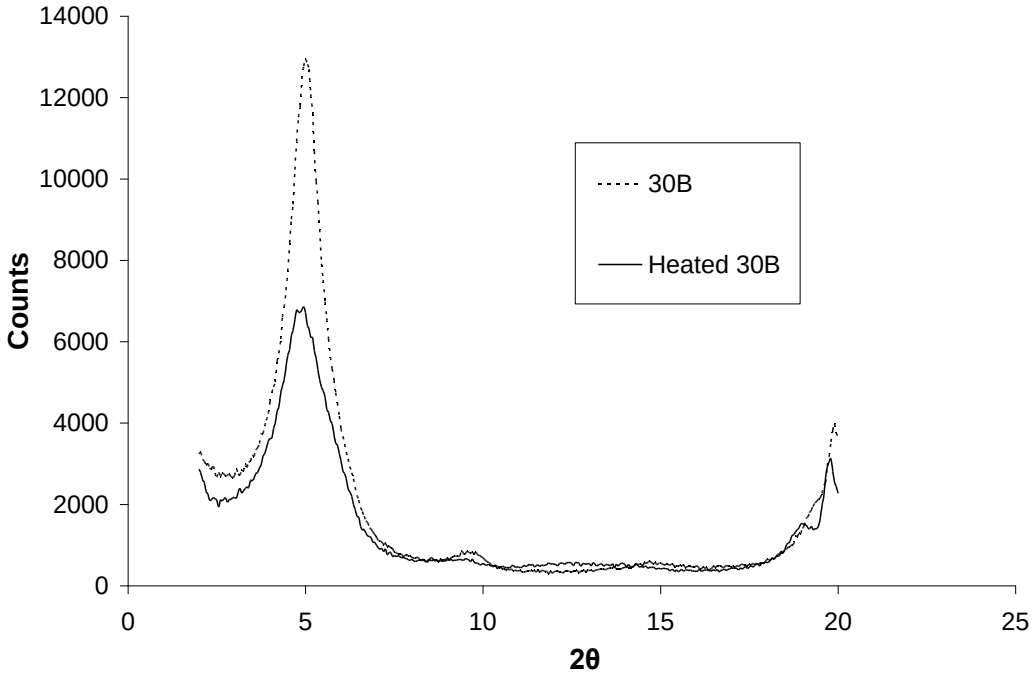

Figure 7 XRD patterns for clay Cloisite 30B before and after heating at 190^{o}C for 10min.

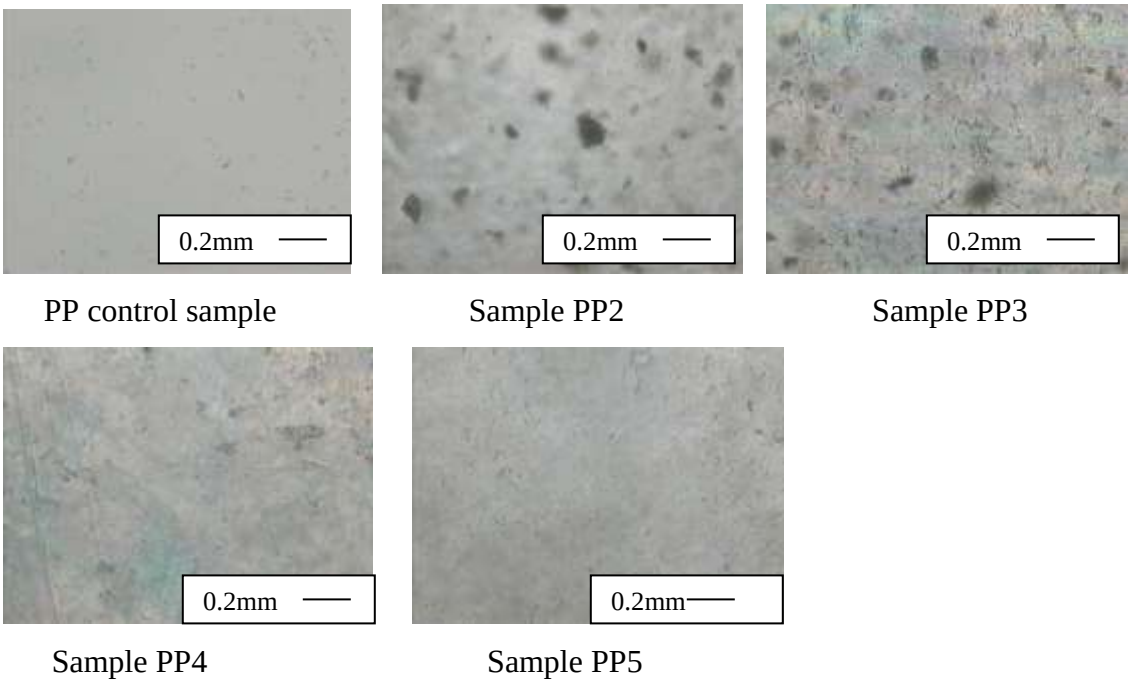

Figure 8 Optical microscope picture of samples PP1 to PP5 (40X)

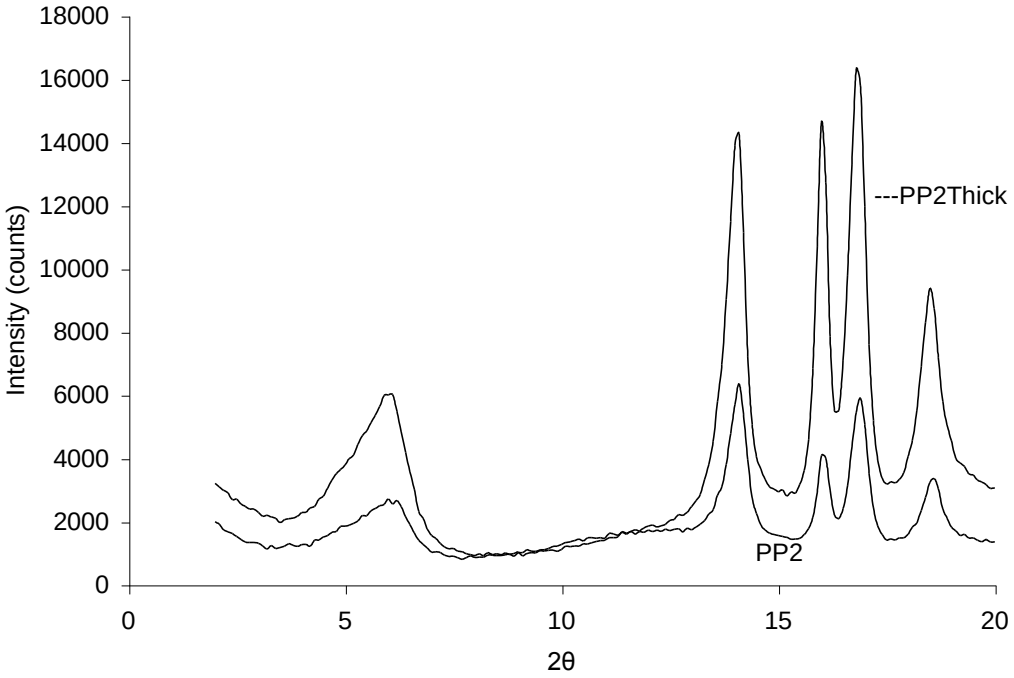

Figure 9 The effect of sample thickness on XRD patterns for compounded sample 2 containing 30B Cloisite clay only